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HIGH TEMPERATURE SULFATION STUDIES IN AN ISOTHERMAL REACTOR: A COMPARISON OF THEORY AND EXPERIMENT

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16. ABSTRACT The paper gives high-temperature isothermal data on sulfur dioxide (SO_2) capture, obtained as a function of temperature, SO_2 partial pressure, and Ca/S molar ratio for a pulverized dolomite (34 micrometer mean size) and a high-purity calcite (11 micrometer mean size). The experimental results indicated that sulfur capture increases approximately linearly with increasing Ca/S ratio and is relatively insensitive to SO_2 partial pressure at the conditions tested. Reaction zone temperature was found to critically influence the overall effectiveness of sulfur capture by sorbent injection; as the local temperature increases, the rates of heterogeneous chemical reaction and diffusion increase, but these are ultimately compensated for by a decrease in initial sorbent surface area due to desurfacing during flash calcination. The experimental results were compared with theoretical predictions using a combined diffusion/heterogeneous chemical reaction model which was developed based on a grain formulation. Initial analysis of various fundamental kinetic studies suggested that the intrinsic chemistry was first order in calcium sites and zero order in SO_2 partial pressure. Model predictions showed good qualitative and quantitative agreement with experimental data. Analysis of temperature profiles from full-scale utility boilers suggests a strong dependency on quench rate in the sulfation zone.

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ABSTRACT

High temperature, isothermal data on SO_2 capture were obtained as a function of temperature, SO_2 partial pressure, and Ca/S molar ratio for a pulverized dolomite (34 micron mean size) and a high purity calcite (11 micron mean size). The experimental results indicated that sulfur capture increases approximately linearly with increasing Ca/S ratio and is relatively insensitive to SO_2 partial pressure at the conditions tested. Reaction zone temperature was found to critically influence the overall effectiveness of sulfur capture by sorbent injection; as the local temperature increases, the rates of heterogeneous chemical reaction and diffusion increase but these are ultimately compensated by a decrease in initial sorbent surface area due to desurfacing during flash calcination.

The results of the experimental studies were compared with theoretical predictions using a combined diffusion/heterogeneous chemical reaction model which was developed based on a grain formulation. Initial analysis of various fundamental kinetic studies suggested that the intrinsic chemistry was first order in calcium sites and zero order in SO_2 partial pressure. Model predictions, based on measured gas temperatures and limestone surface areas without sulfur plus kinetic and diffusion rates derived from previously reported fundamental studies, showed good qualitative and quantitative agreement with experimental data. Analysis of temperature profiles from full-scale utility boilers suggests that effectiveness of dry sorbent injection will depend strongly on the quench rate within the sulfation zone even if sorbent injection is optimized.

INTRODUCTION

Annual sulfur oxide emissions from worldwide industrial sources total about 65 million tons. Because of the relationship between these and acid rain formation, considerable attention is being focused on controls for the combustion of sulfur-containing coals. Extensive early investigations of the dry, calcium-based sorbent injection control technique[1-4] defined the overall process characteristics but yielded conflicting results. Additional high temperature calcination and sulfation data are needed. Previous experimental studies[2] have indicated a weak dependence on oxygen concentration. The effect of SO_2 concentration is complicated by the presence of coupled diffusion and heterogeneous reaction steps; apparent orders of one[5], one-half[2], and zero[6] have been reported. In this study a 65 kW refractory-walled reactor was used to obtain isothermal, sulfur-capture data as a function of temperature, SO_2 partial pressure, and Ca/S molar ratio for well characterized limestone and dolomite sorbents. The experimental results were compared to a grain model which included pore and product layer diffusion as well as heterogeneous chemical reaction.

EXPERIMENTAL SYSTEMS

The calcination and sulfation data were obtained in an isothermal, refractory-walled reactor 3.0 m high with an inside diameter of 15 cm. A natural gas-fired burner is attached to a horizontal extension at the bottom of the furnace to supply hot combustion products which flow vertically upward within the reactor. Independent wall and gas temperature control is provided by a pair of 30 kW natural gas auxiliary burners which are attached to the upper portion of the furnace and fired downward in annular channels around the main combustion chamber.

Suction pyrometers (Pt/Pt-Rh) were used to continuously characterize the reaction zone gas temperature (the combined axial and day-to-day standard deviation was ±16° F).

SO_2 was metered into the inlet gas stream to allow independent control of sulfur partial pressure. Sorbent was metered with a K-tron twin screw auger and transported through an eductor to a water-cooled, "showerhead" sorbent injector located at the bottom of the vertical reaction zone. Cold flow visualization was used to verify that the sorbent was uniformly mixed within two reactor diameters.

The furnace exhaust was continuously monitored for CO, CO_2, O_2, and NO. The SO_2 sample was withdrawn through a controlled temperature, stainless steel, phase discrimination probe and pumped to a DuPont UV 400 Photometric analyzer. Sample conditioning consisted of two glass-wool filters, an electrically-heated line (400 K), two Perma-pure dryers and a 60 micron, stainless steel filter.

Solid sorbent samples for subsequent N_2 BET surface area analysis were collected with a stainless steel, controlled temperature probe followed immediately by a high temperature filter (500 K). At the sampling conclusion, N_2 was used to reduce the filter temperature to ambient and cover all samples. Both probes were located at the end of the controlled temperature zone.

MATHEMATICAL MODELING OF THE SO_2-LIME REACTION

Conceptual Formulation

The heterogenous SO_2-lime reaction can be analyzed by assuming the gaseous reactant, SO_2, undergoes:

- diffusion from the bulk gas to the particle's surface;
- pore diffusion to the particle's interior;
- solid state or ionic diffusion through the product layer ($CaSO_4$); and
- reaction at the product-lime interface.

There is some evidence[2] that the overall reaction

$$CaO + SO_2 + \tfrac{1}{2} O_2 = CaSO_4 \qquad (1)$$

proceeds via a two-step process: reaction of CaO and SO_2 reversibly to form calcium sulfite followed by subsequent oxidation to $CaSO_4$.

Two types of models have been previously applied to the SO_2-lime reaction system in fluidized bed combustion. Ramachandrin and Smith[7], Bhatia and Perlmutter[8] and Simons and Rawlins[9] developed pore models. Pigford and Sliger[10], Hartman and Coughlin[11], and Hartman and Trnka[12] developed grain models. A grain formulation, which assumes that porous lime particles can be represented as conglomerates of nonporous, spherical grains of pure CaO, was adopted for this study based on high resolution STEM photographs of calcined dolomite particles which showed a grain-like structure with 100A cracks. The fluidized bed modeling of Hartman and Coughlin[11] was used as a starting point.

The CaO grains were assumed to react by the shrinking core model. Because of the molar volume difference between CaO and $CaSO_4$ (17 and 46 cm^3 $gmol^{-1}$, respectively), sulfation necessarily causes grain growth and particle porosity reduction. The extended grain radius is a function of the initial radius, r, the radius of the unreacted shrinking core, the molar volumes of CaO and $CaSO_4$, and the porosity of the product.

The following assumptions (with associated justifications) were made in the development of the grain model:

- o the lime particles are fully calcined (preliminary calcination rate calculations);
- o the grains of CaO and MgO are of the same average size (lack of detailed grain size data);
- o the diffusion of reactant to the particle surface is not rate limiting (Damkohler no., Da<0.002);
- o the reaction $CaO + SO_2 + \frac{1}{2} O_2 = CaSO_4$ is irreversible (no reverse reaction rate data available);
- o the intrinsic kinetics of $CaSO_4$ formation are zero order with respect to SO_2 (first order does not agree with available data);
- o the sole reaction product is $CaSO_4$ (the thermodynamically favored product);
- o the CaO grains react by the shrinking core model and the MgO grains do not react ($MgSO_4$ unstable);
- o internal particle temperature gradients are samll (Biot no., Bi <0.07); and
- o excess oxygen is present (measured).

The last assumption allows any reaction rate dependence on oxygen to be included as a constant in the rate term.

Differential Equations

The governing equations were obtained from material balances on the particle and the constituent grains. Starting with the particle and making a steady state approximation, a balance on SO_2 in a spherical shell yielded

$$\frac{d^2C}{dR^2} + \left(\frac{2}{R} + \frac{1}{D_{eff}} \frac{dD_{eff}}{dR}\right) \frac{dC}{dR} - \frac{N}{D_{eff}} = 0 \qquad (2)$$

- At $R = 0$, $\frac{dC}{dR} = 0$ for all time (3)

- At $R = R_p$, $C = C_0$ for all time. (4)

The reaction rate term, N, in Eq.(2) has two different forms depending on whether kinetic or diffusion factors are controlling:

- Kinetic control

$$N = K \cdot A$$

- Diffusion control

$$N = D_s \cdot \frac{dC_i}{dr_i} \cdot A$$

where

$$D_s \cdot \frac{dC_i}{dr_i}\bigg|_r = \frac{(C - C_e)\, D_s}{r(1 - r/r_g')}$$

A material balance on a lime grain yielded the last governing equation:

- Kinetic control

$$\frac{dr}{dt} = - \frac{M_{co}}{\rho_{co}} K \qquad (5)$$

-Diffusion control

$$\frac{dr}{dt} = - \frac{M_{co}}{\rho_{co}} \cdot D_s \cdot \frac{dC_i}{dr_i}\bigg|_r \qquad (6)$$

o At $t = 0$, $r = r_g$ for all R

Solution Procedure

The solution was obtained by writing Eq.(2) in finite difference form and guessing an initial concentration profile for the particle.

Based on the concentration and product layer thickness at each node, diffusion or kinetic control is determined (greatest resistence). Solution is by Newton's method. When a converged concentration profile is obtained, the shrinking core radius of each grain is decreased by an amount determined from Eq.(5) or (6). The above cycle is repeated until the reactor residence time has elapsed. An overall reactor material balance is used to calculate the free stream SO_2 concentration at each time step and to compute the reduction of gas phase SO_2 by the sorbent particles at each axial location within the reactor. Overall SO_2 capture is based on comparison of entrance and exit concentration.

Physical Parameters

Four parameters are relevant to the grain model: the intrinsic chemical rate constant, K; the effective pore diffusivity, D_{eff}; the diffusion coefficient for the solid product layer, D_s; and the grain radius, r_g. The first three were based on literature data and the last, r_g, was computed from measured surface areas.

The chemical rate constant was determined from the conversion versus time data of Borgwardt[5] as suggested by Bhatia and Perlmutter[8]. By extrapolating his rate data to time zero and plotting the results in Arrhenius form, the following expression for K was obtained:

$$K = 0.327\ (10^{-5})\ \exp\ (-6445./T)\ \text{gmol cm}^{-2}\ \text{sec}^{-1}$$

The effective pore diffusivity was calculated as

$$D_{eff} = De_x^2$$

where D is the combined diffusivity given by

$$D = (D_m^{-1} + D_k^{-1})^{-1}.$$

The bulk diffusivity, D_m, for the binary pair SO_2-air was obtained from the Chapman-Enskog theory as

$$D_m = \exp(1.66 \ln T - 11.3), \text{ cm}^2/\text{s}.$$

The Knudsen diffusion coefficient, D_k, is given by

$$D_k = 19400 \frac{e_x}{S\rho}\left(\frac{T}{M}\right)^{\frac{1}{2}}, \text{ cm}^2/\text{s}$$

where

e_x = the porosity of the reacting porous lime,

S = the BET surface area, cm^2/g,

ρ = the bulk density of the calcined stone, g/cm^3, and

M = the molecular weight of the gaseous reactant.

The solid product-layer diffusion coefficient, D_s, was obtained by fitting the rate data of Borgwardt[5] with the grain model. The Arrhenius expression for D_s is

$$D_s = 0.0124 \exp(-12200/T), \text{ cm}^2/\text{s}.$$

The grain radius was estimated from BET surface area data by the expression,

$$r_g = \frac{3}{S\rho_{CO}}$$

A BET surface area of 10 m^2/g corresponds to r_g = 0.09 microns.

DISCUSSION OF RESULTS

Intrinsic Order of the SO_2-Lime Reaction

Previous fundamental experimental studies have indicated apparent orders of zero[6], one-half[2], and one[5] for the dependence of capture on SO_2 concentration. An examination of each of these studies, using the grain model developed in this work (incorporating pore diffusion, product layer diffusion and zero order intrinsic chemical kinetics), indicated that the apparently conflicting results are the result of competition between kinetic and diffusional effects; the zero order intrinsic chemical kinetics incorporated into the current model are required to rationalize all of the different results. Physically, the zero order could be due to limited CaO site availability.

The extensive results of Borgwardt[5] indicate an apparent first order dependence on SO_2 with very large (720 micron) lime particles. The rate of the reaction at various SO_2 concentrations was determined when the overall molar conversion of the particles to product reached 0.105. When the lime particle diameter is large, the deposition of product is confined to the outer portions of the stone due to significant pore diffusion resistance. In addition, the local conversion near the particle surface exceeds 0.105 and product layer diffusion cannot be ignored. The model correctly predicts that under these conditions the apparent order with regard to SO_2 concentration is 1.0 (because pore and product layer diffusion resistances are large relative to intrinsic chemical resistance).

Coutant and coworkers[2] also studied concentration effects with intermediate sized particles and determined an apparent half order dependence on SO_2. Their rate measurements with 90 micron particles were extrapolated to time zero, thereby obviating the effect of product layer

diffusional resistance. According to the model, the concentration gradient within a particle of this size is very steep due to pore diffusion resistance. For this reason, first order diffusional effects again influence the rate of the reaction although here they are not totally dominant relative to intrinsic kinetics. The model correctly predicts an apparent 0.46 order for these conditions.

Ishihara[6] reported data for very small (10 micron) particles. His rate measurements, extrapolated to time zero, indicated an initial zero order SO_2 dependence and for these conditions, the model correctly predicts a zero order dependence due to kinetic control.

Influence of Reaction Zone Temperature

Initially the influence of reaction zone temperature on calcination and subsequent sorbent activity was defined. Sorbent was injected at the reaction zone entrance (furnace bottom); solid samples were collected at the controlled temperature zone (470 msec later) for surface area characterization. No SO_2 was present; the surface areas were for unreacted calicum oxide. Two sorbents were used: high-purity, large-grain limestone (Vicron 45-3, 11μ mean size) and 56% $CaCO_3$ dolomite (mean size of 34μ).

Figure 1a illustrates surface area development at constant temperature (1255K) as calcination proceeds (extent of calcination shown in parentheses). Limestone surface area rose rapidly, peaked and then decreased with increased exposure time; dolomite areas were essentially constant after the initial rise. Initial calcination was very rapid (<0.25 s). Figure 1b shows the reactor temperature effect at 470 msec. Surface areas near 30 m^2/g (50 m^2/g calcine) were achieved for both limestone and dolomite at low temperatures with partial calcination. Surface area

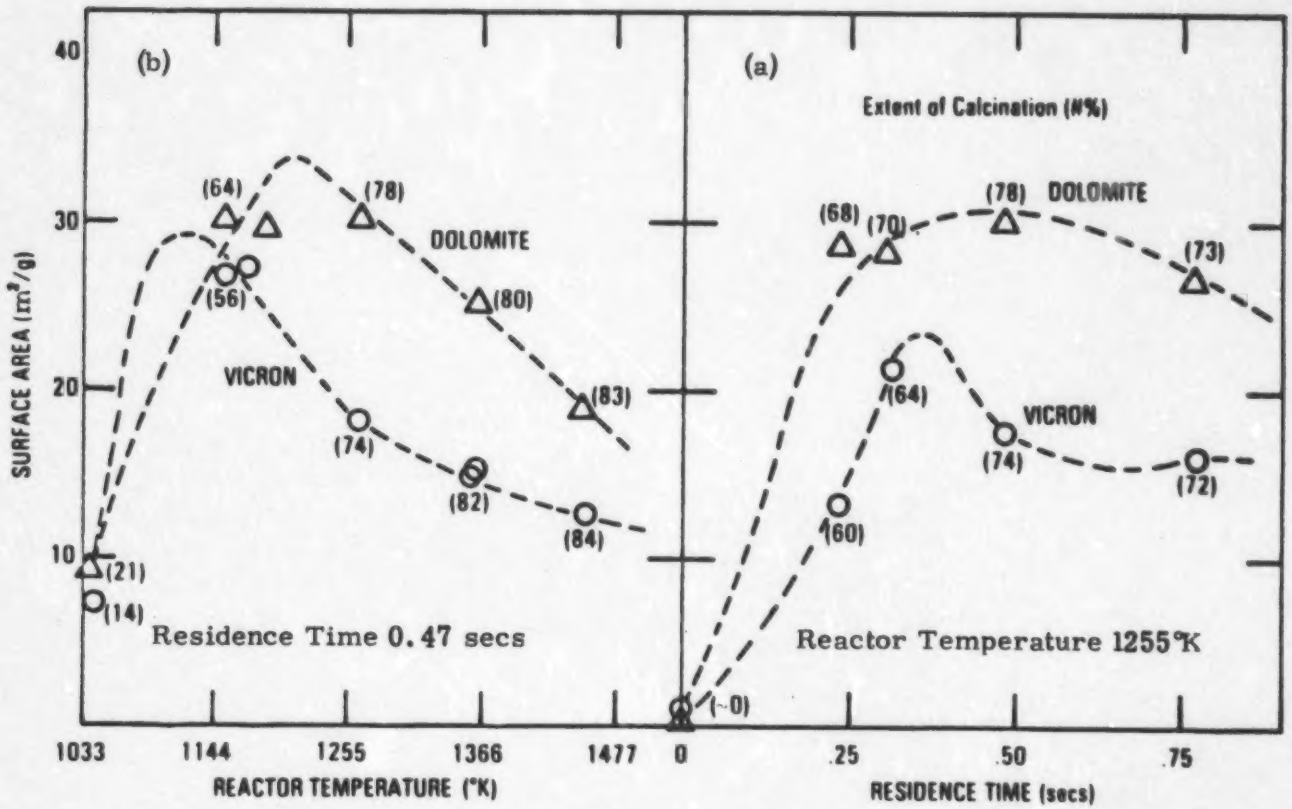

Figure 1. Surface area as a function of reactor temperature (a) and time (b) for flash calcined Vicron 45-3 and dolomite.

decreased rapidly with increased calcination temperature and to a lesser extent exposure time. (MgO and CaO in dolomite were assumed to contribute surface areas based on their molar volumes and weight fractions.)

Corresponding SO_2 capture data vs. reactor temperature (Fig. 2) indicate 41±1% capture was achieved in 470 msec with dolomite. Limestone captures were lower (maximum 23±1%) and decreased as reaction zone temperature increased. Model predictions (solid lines) were based on measured temperatures and surface areas. In-site particle size was based on data of Seeker and Cole[13] (limestone 5μ, dolomite 34μ). No adjustments were made to improve experimental/model agreement; all diffusion and chemical rates were based on prior fundamental data. Agreement with limestone (Vicron) was good; capture decreases with increasing temperature because the available surface area decrease exceeds increased chemical and diffusion rate effects. Poor agreement with dolomite is probably due to improper accounting for MgO effects which are not well understood at present.

Influence of SO_2 Concentration

Capture was relatively insensitive to the SO_2 partial pressure (Fig. 3) with both sorbents in agreement with recent pilot-scale results[14]. The molar ratio of Ca sites to SO_2 was held constant at 2.0; as SO_2 increased, the corresponding concentration of sorbent also increased due to the constant Ca/S ratio. If the intrinsic chemical kinetics were first order in SO_2 as previously reported, then both diffusion and kinetic effects would produce a linear capture dependence on SO_2. The solid lines (model predictions) include consideration of pore diffusion, product layer diffusion and heterogeneous reaction at the calcium oxide interface. In general, the overall reaction rate is initially controlled by $CaSO_4$ formation at the

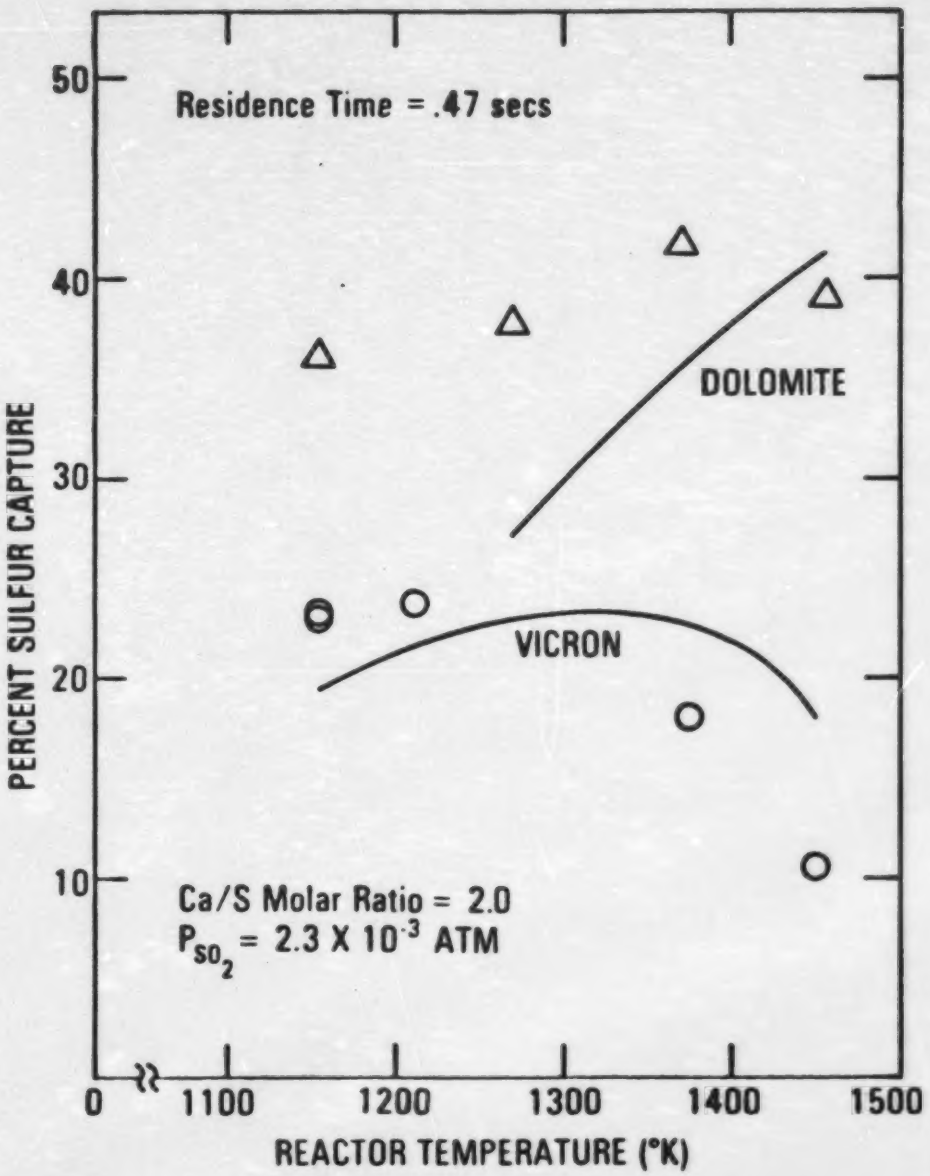

Figure 2. Percent capture as a function of temperature for Vircon 45-3 and dolomite.

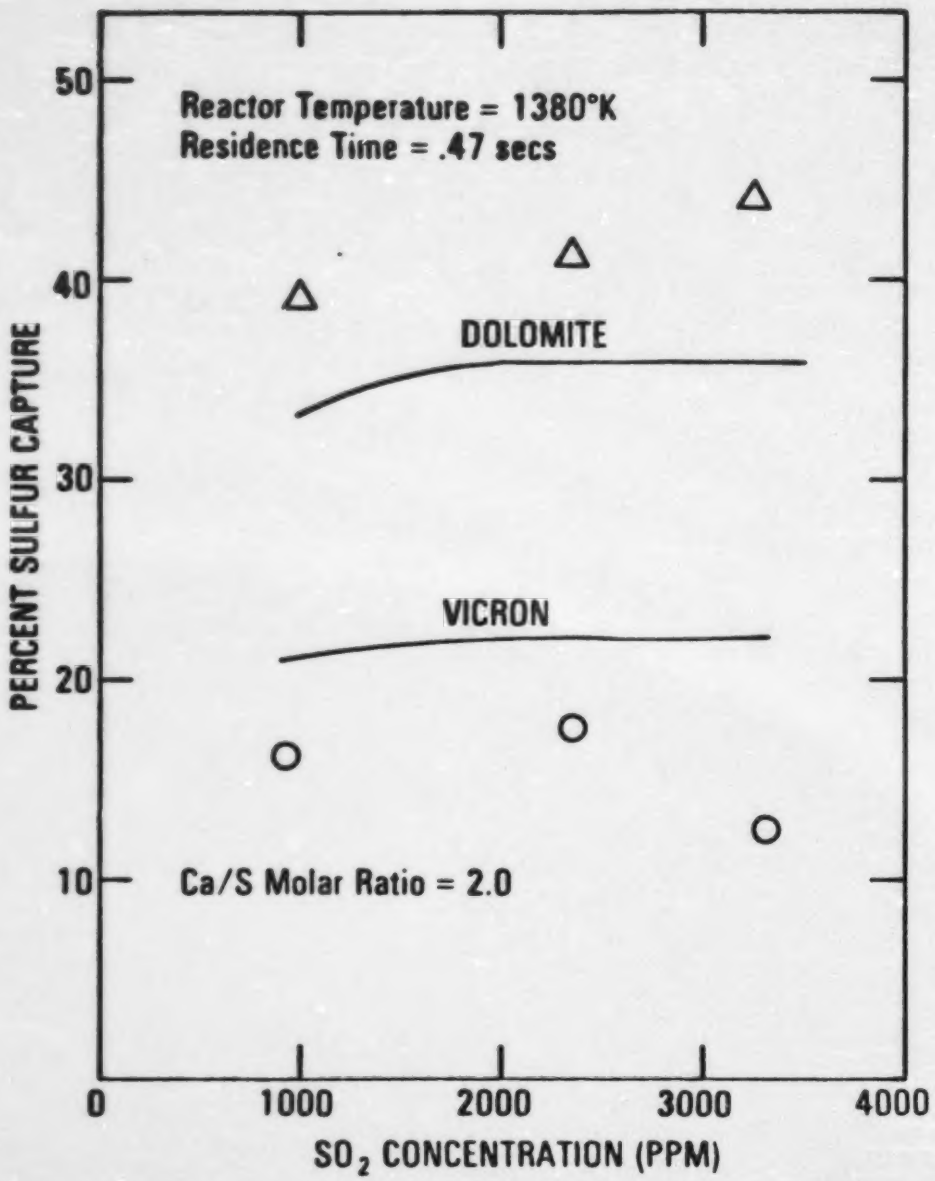

Figure 3. Percent capture as a function of SO_2 concentration for Vicron 45-3 and dolomite.

$CaSO_4$/CaO interface (kinetic control). However, the $CaSO_4$ layer ultimately becomes thick enough that product layer diffusion progressively controls at each radial position within a particle. Under the conditions of these experiments (relatively short times and moderate surface areas), the sulfation processes are primarily dominated by kinetic control. Thus, the grain model with zero order chemistry predicts insensitivity of capture to SO_2 in direct agreement with the data. Note, however, under other conditions (e.g. high extents of sulfation, low SO_2 partial pressures, etc.) the model predicts a much steeper dependence of capture on SO_2 concentration because of more diffusion control.

Ca/S Molar Ratio

Increasing the Ca/S ratio at constant SO_2 (2300 ppm) resulted in increased sorbent site availability and improved SO_2 capture (Fig.4). Again dolomite capture was consistently above limestone. The approximately linear dependence of capture on Ca/S suggests the overall process is first order in available calcium sites. Again the solid lines indicate model predictions without any adjustments to improve agreement.

CONCLUSIONS

Fundamental sulfation data (Borgwardt[5]) can be extrapolated to coal combustion conditions and used with a diffusion/heterogeneous kinetics model to predict SO_2 capture by calcium sorbents. Capture increases approximately linearly with increasing Ca/S ratio and is relatively insensitive to SO_2. Temperature has a complex influence on SO_2 capture because it controls sorbent reactivity (as characterized by surface area) and both diffusion and chemical rates. Increasing temperature increases both kine-

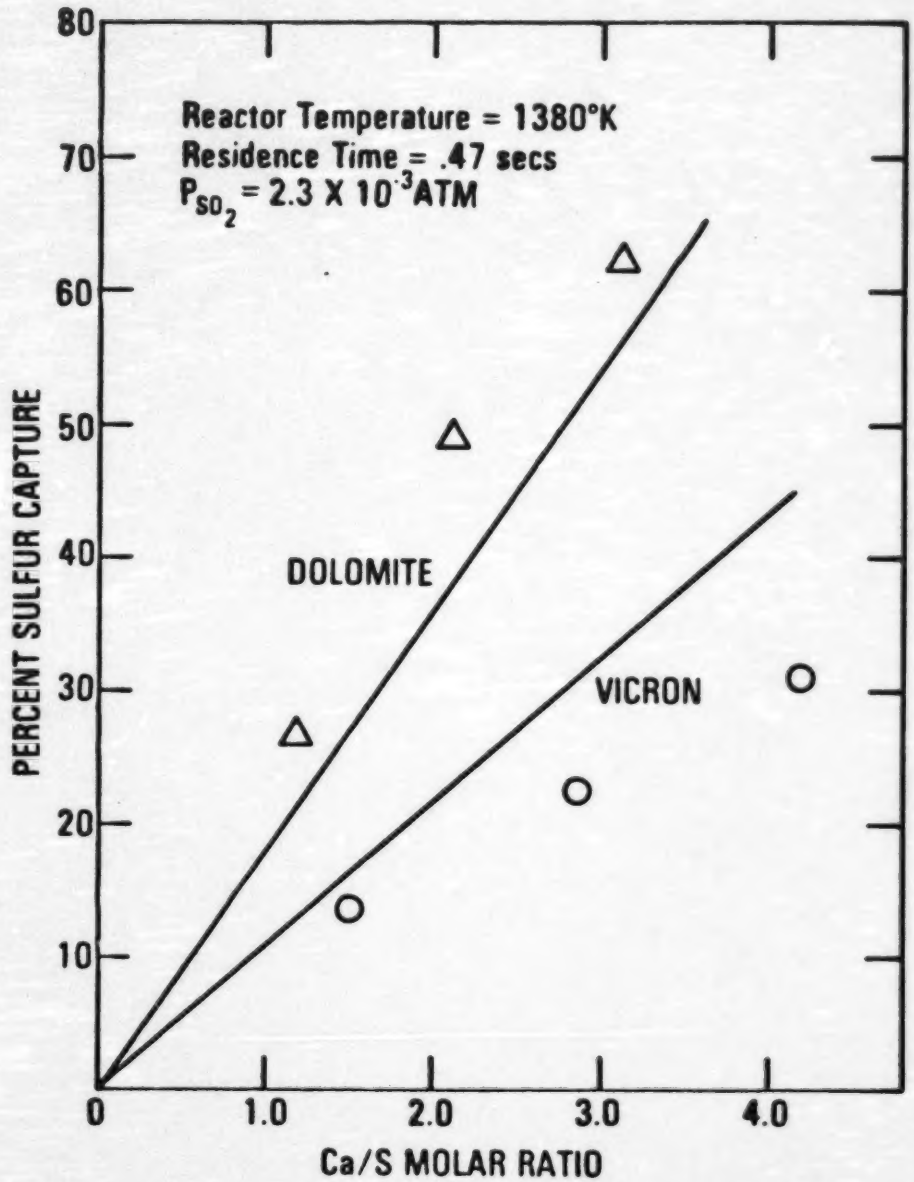

Figure 4. Percent capture as a function of Ca/S molar ratio for Vicron 45-3 and dolomite.

tic and diffusion rates; and significantly decreases sorbent surface area.

The model can be used to predict sulfur capture with industrial conditions (Fig. 5). Fig. 5a shows the influence of sorbent injection location. Sulfation was assumed to begin once the sorbent particle cooled below 1500 K (2250° F) for a quench rate (from 1500 to 1250 K) of 208 K/sec. Surface area was based on injection temperature. Decreasing injection temperature increased predicted capture (because it increased available surface area) until the point at which the residence time in the sulfation zone dramatically decreased. Under optimum conditions, the capture with dolomite was predicted to exceed 50 percent at Ca/S of 2.0.

Figure 5b shows the influence of varying sulfation zone (1500 to 1250 K) quench rate with Ca/S of 2.0 and 1450 K (2150° F) injection temperature. These predictions suggest sorbent effectiveness will depend strongly on the boiler heat transfer rate within the sulfation zone even if both the sorbent and injection point are optimized.

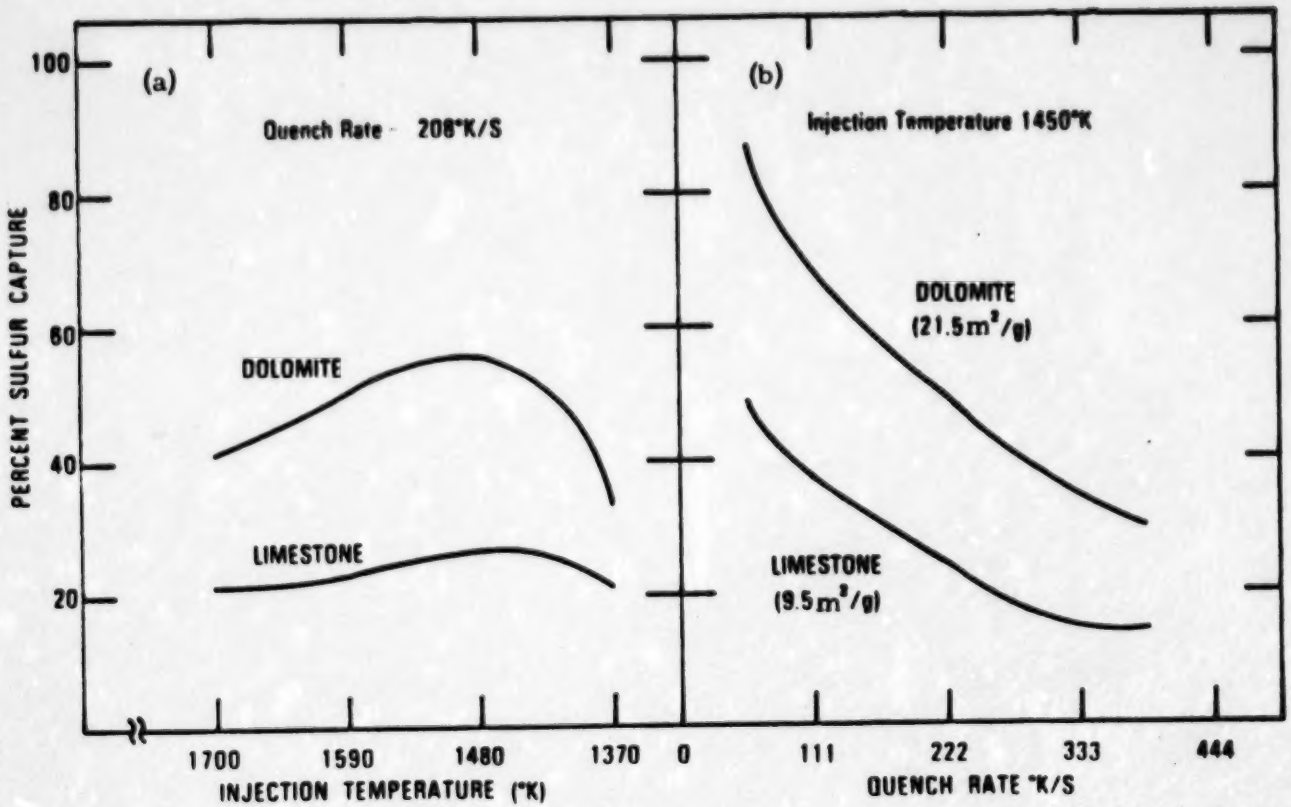

Figure 5. Model predictions showing the effect of injection temperature (a) and quench rate (b) on capture for Vicron 45-3 and dolomite.

NOMENCLATURE

A = Interfacial area available for reaction per unit volume of porous lime, $cm^2\ cm^{-3}$

C = Concentration of SO_2 at some radius R, gmol cm^{-3}

C_e = Equilibrium concentration of SO_2, gmol cm^{-3}

C_i = Concentration of reactant gas in the product shell, gmol cm^{-3}

D_{eff} = The effective diffusivity of the reactant gas in porous lime, $cm^2\ s^{-1}$

D_s = Product-layer-diffusion coefficient, $cm^2\ s^{-1}$

e_x = Porosity of the reacting porous lime

K = Zero-order rate constant, gmol $cm^{-2}\ sec^{-1}$

M_{co} = Molecular weight of CaO

N = The rate at which reactant is consumed per unit volume of porous solid, gmol $cm^{-3}\ sec^{-1}$

r = Radius of the unreacted core of CaO, cm

r_g = Initial grain radius, cm

r'_g = Extended grain radius, cm

r_i = Radial coordinate within the product shell, cm

R = Radial distance inside the particle, cm

R_p = Particle radius, cm

t = Time, seconds

ρ_{co} = Density of CaO, g cm^{-3}

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